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Solvent Effect on the Redox Potentials of Tetraethyl Ammonium Hexacyanomanganate(III): A Computational Study

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The present research includes calculations and computations of tetraethyl ammonium hexacyanomanganate(III) $(Mn(CN)_6{}^{3-}$ electrode potentials in three solvents AC, DMSO and MeOH. For this purpose, the DFT-B3lyp calculations with the 6-311+g** basis set were utilized. The calculated values were compared with the experimental data that obtained by cyclovoltametry (CV). The observed and the calculated changes in the reduction potential of the complexes differed from those of the reference compound (BBCr).

Keywords: Mn(II), PCM, Solvent effect, DFT, $E_{1/2}$

1. INTRODUCTION

Transition metal complexes have been studied as catalysts in organic and inorganic redox and electrochemical reduction reactions[1-4].The electrochemical properties of several transitional metal and complexes were studied intensively[5-11].They play a crucial role in the activity of several reactions, such as, activity of hydrogenase [12] or electrochemical reaction of alkyl and aryl halides[13-18].Cyclic voltametry has been a useful instrument to study the mechanism of the catalysis property of metal complexes and their reactivity[2,4].The electrochemical methods also provide highly valuable information regarding catalytic processes since catalytic conversions are frequently accompanied by change in the structure of the complex and the oxidation state of the metal, however, the electrochemical approaches for these purposes have not been fully explored[19, 20]. The ability to calculate redox potentials accurately using the theoretical methods would be advantageous in a number of different areas, particularly where the experimental measurements are difficult, due to the complex chemical equilibiria and the reactions of the involved chemical species. Recently, a number of reports, dealing with the electrode potential calculation of several biomolecules, have been published in the literature [21-23].Actually, the resulting date illustrated that the method was likely to be useful the predictor of biomolecules electrode potentials in diffent aprotic solvents [24]. Conversely, the solvent effect on dissolution or on a chemical reaction can be predicted quantitatively from knowledge of the solvation energies of the relevant solutes. During the last two decades, studies on ion solvation and electrolyte solutions have made remarkable progress by the interplay of experiments and theories. Experimentally, X-ray and neutron diffraction methods and sophisticated EXAFS, IR, Raman, NMR and dielectric relaxation spectroscopies have been used successfully to obtain structural and/or dynamic information about ion-solvent and ion-ion interactions[25].

Our goal in the present study is to investigate metal-mediated deduction processes by theoretical methods. The redox reactions of $Mn(CN)_6^{3-}$ lead to $Mn(CN)_6^{4-}$, the potassium salt of which is known as $K_2Mn(CN)_6$ which is obtained by oxidation of $K_3Mn(CN)_6$ with NaCl in dimethyl foramide[26] and found to be sensitive to hydrolysis and light. It decomposes swoly in many solvents and both of them are stable in water only in the presence of excess cyanid ions.

The redox potentials for reduction of $(et_4N)_{3Mn}$ $(CN)_6$ to $(et_4N)_{4Mn}$ $(CN)_6$ vary considerably with the nature of the solvent. As in previous studies all potentials are referred to bis-biphenylchromium(I)/ bis biphenylchromium(0) [BBCr(I) /BBCr(0) as reference redox system[27].

2. COMPUTATIONAL DETAIL

2.1. Computational Program

A Pentium IV personal computer system was used and the initial geometry optimization was performed with hyperchem(version 10) for all the abinitio calculations, also Gaussian 03 was employed.

In this study, the chemical structure of all of the complexes were optimized using Gaussian 03 program at DFT-B3LYP/ 6-31G* level of theory and the half-ware potentials were obtained from output results.

2.2. Calculation method

The Mn(II) complex with CN ligands were oxidized in Acetonitril, DMSO and MeOH, by a one-electron metal centered process to six-coordinat Mn(III) species formulated as $Mn(III)L_6$ according to redox reaction [28]:

$$Mn(III)_{sol} + e^- \rightarrow Mn(II)_{sol} \qquad (1)$$

In the present study, the gas-phase contributation to the Gibbs energy, $\Delta G°_{gas}$ and salvation energy, $\Delta G°_{solv}$ was determined from abinitio calculations. The Gibbs free energy change for reaction 1 can be computed by the thermodynamic cycle depicted in Figure 1. The different between the electrode potentials of the two species can be obtained from the equation 2.

$$\Delta G° = nf\,(E°_c - E°_a) \qquad (2)$$

Where ΔG° is total free energy for reaction, $E°_a$ is the experimental potential for a reference molecule, $E°_c$ is the calculated potential and F is the faraday constant ($F = 96491 Cmol^{-1}$).

Experimenral values E°exp were reported in reference [29].

$$\begin{tikzcd}
Mn^{3+}_{(g)} + e^- \arrow[r, shift left, "\Delta G_{(g)}"] \arrow[d, "\Delta G_{(solv, red)}"'] & Mn^{2+}_{(g)} \arrow[l, shift left] \arrow[d, "\Delta G_{(solv, ox)}"] \\
Mn^{3+}_{(sol)} + e^- \arrow[r, shift left, "\Delta G_{(tot)}"] & Mn^{2+}_{(sol)} \arrow[l, shift left]
\end{tikzcd}$$

Figure 1. The thermodynamic cycle, proposed for calculation of ΔG_{tot}

3. RESULTS AND DISCUSSION

3. 1. The electrochemical properties of the studied complexes

The computational values of ($E_{1/2}$) and their experimental data in three solvents along with three different methods are listed in table 1-3.

Table 1.Gibbs energy and half-wave potentials of studied complexes for both reduced(Mn^{2+}) and oxidized (Mn^{3+}) forms in the gas and solution phases calculated using 6-311+g** basis set at HF level of theory with CPCM model.

Solvent	$G_{Mn^{3+}}$ **(g)**	$G_{Mn^{2+}}$ **(g)**	$G_{Mn^{3+}}$ **(s)**	$G_{Mn^{2+}}$ **(s)**	ΔG_{rea} **(tot)**	$E_{\frac{1}{2}}$ **Theory**	$E_{\frac{1}{2}}$ **Exp**
AN	1703.29266	-1702.5248	-1703.180183	-1703.86711	-92714.2709	-0.837	-0.840
DMSO	-1703.29266	-1702.5248	-1703.82885	-1703.87383	-118089.725	-0.970	-0.919
Me OH	-1703.29266	-1702.5248	-1703.83180	-1703.87506	-113579.117	-0.282	-0.233

The Gibbs energy is in atomic units. Hartree ($1 Hartree = 2625488.7 jmol^{-1}$ and $E_{1/2}$ is in terms of volt.

The cyclic voltammetric curves for the electrochemical oxidation of the study`s Mn(II) complexes exhibit a redox couple at potentials in the range of -0.840v in AC, -0.919v in DMSO and -0.233v in MeOH[29]. Electrode potentials of the Mn(III) and Mn(II) complexes were calculated in three solvents AC, DMSO and MeOH. Results show, the half -wave potentials of Mn complexes are near to experimental results and that the $E_{1/2}$ for methanol and DMSO are less that of AC.

Table 2 .Gibbs energy and half-wave potentials of studied complexes for both reduced(Mn^{2+}) and oxidized (Mn^{3+}) forms in the gas and solution phases calculated using 6-311+g** basis set at HF level of theory with IEFPCM model.

Solvent	$G_{Mn^{3+}}$ **(g)**	$G_{Mn^{2+}}$ **(g)**	$G_{Mn^{3+}}$ **(s)**	$G_{Mn^{2+}}$ **(s)**	ΔG_{rea} **(tot)**	$E_{\frac{1}{2}}$ **Theory**	$E_{\frac{1}{2}}$ **Exp**
AN	-1703.29266	-1702.95248	-1703.82432	-1703.86693	-111854.1637	-1.03	-0.840
DMSO	-1703.29266	-1702.95248	-170.82881	-1703.87368	-117808.797	-0.967	-0.919
Me OH	-1703.29266	-1702.95248	-1703.83175	-1703.87485	-113161.6626	-0.277	-0.233

Table 3 .Gibbs energy and half-wave potentials of studied complexes for both reduced(Mn^{2+}) and oxidized (Mn^{3+}) forms in the gas and solution phases calculated using 6-311+g** basis set at HF level of theory with COSMO model.

Solvent	$G_{Mn^{3+}}$ **(g)**	$G_{Mn^{2+}}$ **(g)**	$G_{Mn^{3+}}$ **(s)**	$G_{Mn^{2+}}$ **(s)**	ΔG_{rea} **(tot)**	$E_{\frac{1}{2}}$ **Theory**	$E_{\frac{1}{2}}$ **Exp**
AN	-1703.29266	-1702.95248	-1703.84545	-1703.90653	-160389.151	-1.539	-0.840
DMSO	-1703.29266	-1702.95248	-1703.84746	-1703.90800	-158955.628	-1.394	-0.919
Me OH	-1703.29266	-1702.95248	-1703.85442	-1703.91628	-162395.032	-0.788	-0.233

3.2. Solvent effect on oxidation potentials

The complexation **o**f a solvated metal ion with a ligand (complexing agent) corresponds to the substitution of the solvent molecules existing in the first solvation sphere with the molecules or ions of the ligand in solution.

Here, the metal ion-solvent interaction competes with the metal ion-ligand interaction. Solvent molecules also interact with the free ligand and the ligand coordinated to the metal ion, affecting the reactivity of the ligand. Thus, the stability of a metal complex is easily influenced by solvent. In ion solvation, the solvent molecules approach a cation with their negative charge and approach an anion with their positive charge (Fig. 2). Therefore, cation solvation is closely related to the electron pair donor capacity or Lewis basicity of solvents and tends to become stronger with the increase in donor number (DN). On the other hand, the anion solvation is closely related to the electron pair acceptability or Lewis acidity of solvents and tends to become stronger with the increase in acceptor number (AN)[25].

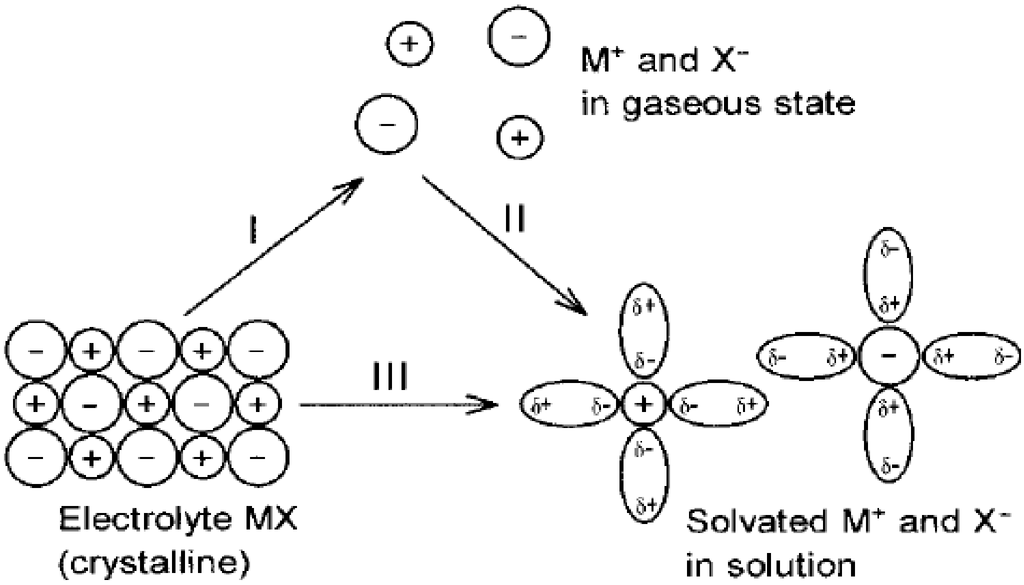

Figure 2. Dissolution process of crystalline electrolyte MX into a solvent

The cyclic voltamograms for electrochemical reduction of the studies complexes show a redox couple at the potentials in -0.233, -0.919 and -0.840v in three solvent for MeOH, AC and DMSO, respectively, which can be attributed to the reduction of metal center [30].

Also, $E_{1/2}$ value show that in DMSO as solvent appear in more negative potentials relative to another two solvents. The dimethyl solfoxide with higher donor number (D. N. =29.8) and acceptor number (A. N. =19.3)[31] was coordinated to the complexes and stabilized the Mn(III) cation.

In liquid solutions, a ground- state donor or acceptor molecule is free to approach an excited acceptor or donor by random walk. After the encounter between donor and acceptor, a light-emitting intermediate is sometimes formed. This intermediate is usually called an excited charge-transfer complex in which the change and electronic excitation is shareed by the donor- acceptor pair. Excited charge- transfer complexes are very important intermediates in the electron transfer quenching process and many photochemical reactions. The polarity of the solvent will affect the electronic and geometric structure. The excited charge-transfer complexes will become more polar with increasing solvent polarity [32, 33] in table 1-3. Withil, for redox couples of metal ions ($M^{n+}/M^{n'+}$ where n>n'), the standard potentials usually shift to negative direction with the increase in permittivity or in Lewis basicity of solvents. This is because M^{n+} is usually more stabilized than $M^{n'+}$ by its transfer from solvent of lower permittivity to that of higher permittivity or from solvent of lower basicity to that of higher basicity.

3.3. The effects of used methods on oxidation potentials

The Gibss energies at 298.15K, Solvation energies, and half-wave potentials were calculated using Polarisable Continuum Models (PCM).

From tables 1-3, it could be inferred that differences between computational and experimental values of $E_{1/2}$ in CPCM method is in the range of 0.003-0.049v and IEFPCM method is 0.19-0.044v, while that of COSMO method is 0.699-0.430v.Table 4 showed $E_{1/2}$ values from left to right across a period in the trend of COSMO<IEFPCM< CPCM.

Table 4. Comparison of results of half-wave potentials calculated with experimental in three methods CPCM, IEF and COSMO in solvents Acetonitril, Dymethylsolfixide and Methanol

Solvent	$E_{\frac{1}{2}}$ **COSMO**	$E_{\frac{1}{2}}$ **IEFPCM**	$E_{\frac{1}{2}}$ **CPCM**	$E_{\frac{1}{2}}$ **Exp**
AN	-1.539	-1.03	-0.837	-0.840
DMSO	-1.394	-0.967	-0.970	-0.919
Me OH	-0.788	-0.277	-0.282	-0.233

3.4. Geometry optimization

The geometrical optimization was calculated. The bond lengths and bond angles of the studied compounds were optimized wchich are shown in table 5 and 6. These show the significant changes of bond length and bond angel Mn^{2+} in relation to Mn^{3+}. The bond length Mn^{2+}— C from 2.360 and 2.479 A° in equoterial and axial position as compared to Mn^{3+}— C bond lengths 2.145 and 2.125 are long that it is agreement with our anticipation from Mn^{3+} cation because with increase of positive charge central metal in complexes decreases the bond length Fig 3.

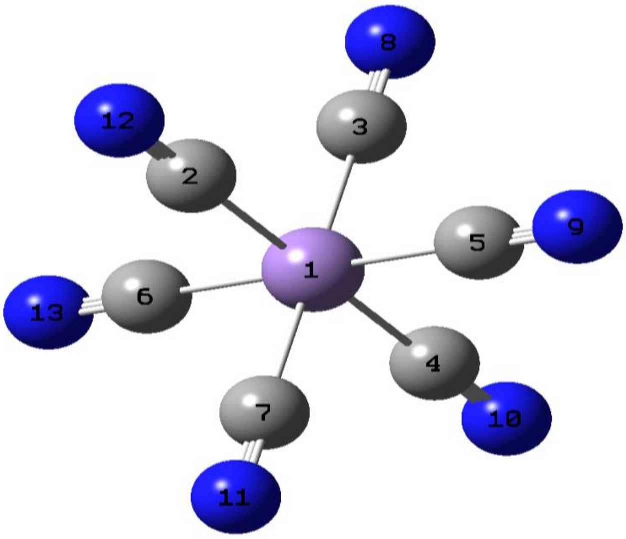

Figure 3. optimized complex of $Mn(CN)_6^{3+}$ with symbol of atoms

Table 5.The bond lengths of Mn^{2+} and Mn^{3+} optimized

Bond lengths ($\dot{A}$ **)**	Mn^{2+}	Mn^{3+}
r_{mn-c_1}	2.360	2.145
r_{mn-c_2}	2.360	2.145
r_{mn-c_3}	2.360	2.145
r_{mn-c_4}	2.360	2.145
r_{mn-c_5}	2.479	2.125
r_{mn-c_6}	2.479	2.125
$r_{c_1-N_1}$	1.166	1.158
$r_{c_2-N_2}$	1.166	1.158
$r_{c_3-N_3}$	1.166	1.158
$r_{c_4-N_4}$	1.166	1.158
$r_{c_5-N_5}$	1.168	1.158
$r_{c_6-N_6}$	1.168	1.158

Table 6. The bond angles of Mn^{2+} and Mn^{3+} optimized

Bond lengths ($\dot{A}$ **)**	Mn^{2+}	Mn^{2+}
$\theta_{C_1-mn-c_2}$	90.00	89.99
$\theta_{C_1-mn-c_3}$	180.0	180.0
$\theta_{C_1-mn-c_4}$	90.00	90.00
$\theta_{C_1-mn-c_5}$	89.99	90.00
$\theta_{C_1-mn-c_6}$	90.00	89.99
$\theta_{C_2-mn-c_3}$	90.00	90.00
$\theta_{C_2-mn-c_4}$	180.0	180.00
$\theta_{C_2-mn-c_5}$	90.00	89.99
$\theta_{C_2-mn-c_6}$	89.99	90.00
$\theta_{C_3-mn-c_4}$	90.00	89.99
$\theta_{C_3-mn-c_5}$	90.00	89.99
$\theta_{C_3-mn-c_6}$	89.99	90.00
$\theta_{C_4-mn-c_5}$	89.99	80.00
$\theta_{C_4-mn-c_6}$	90.00	89.99
$\theta_{C_5-mn-c_6}$	180.0	180.0

4. CONCLUSIONS

The electrochemical behavior of MnL6n+ was studied in AN, DMSO and Me|OH solvents, with 14.6, 29,8 and 32 donor numbers, respectively[34]. We expect good correlation between the redox potentials and solvent properties. The results show that the cyclic voltammograms of studied complexes are solvent dependent. However no clear trend between the CV and the properties of the solvents, such as the donor number of solvent was found out [34]. In this study CV was carried out on Mn (III) reduction and determined the half-wave potentials ($E_{1/2}$).

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